THE KINETICS OF THERMAL DECOMPOSITION OF SILVER OXALATE

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ABSTRACT

The kinetics of thermal decomposition of silver oxalate under conditions of photographic darkness is studied. The kinetic findings corroborate the idea of the reaction mechanism as a process of generation and growth of submicroscopic three-dimensional reaction nuclei.

Although the kinetics of silver oxalate decomposition has now /1103* been studied in a number of papers (Macdonald [Ref. 2, 3, 6], Macdonald and Hinshelwood [Ref. 1], Benton and Cunningham [Ref. 5], Macdonald and Sandison [Ref. 4]), nevertheless up to the present there has been no unified opinion either regarding the mechanism by which the reaction propagates in solid oxalate of silver or even regarding the purely formal kinetics of this reaction.

The inconsistency of the experimental findings and the conclusions drawn from them should be attributed chiefly to the sensitivity of the silver oxalate reaction toward a number of factors.

Thus, Macdonald and Hinshelwood [Ref. 1] found that silver oxalate precipitated in an excess of sodium oxalate decomposes faster than the substance deposited in an excess of silver nitrate. Macdonald [Ref. 2] also ascertained that the reaction is severely inhibited if the silver oxalate is dispersed in oil or melted paraffin. Dispersion in gelatine leads to the same effect, but a less pronounced one. Macdonald and Sandison [Ref. 4] cite data which show that paraffin (purified and un-purified), dichlorobenzene, "liquid paraffin", nitrobenzene, and dibenzyl inhibit the reaction (in comparison with decomposition under vacuum), while phenol, sucrose or glucose sirup, aniline, and benzaldehyde increase the rate of disintegration.

We should note that, of the substances studied by Macdonald and Sandison, the reducing agents accelerate the reaction, but the oxidizing

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* Numbers in the margin indicate pagination in the original foreign text.

agents which they investigated inhibit the reaction. Oxygen inhibits (Macdonald and Hinshelwood [Ref. 1]), but mercury vapors somewhat accelerate the reaction. Ultraviolet light has an accelerating effect. Benton and Cunningham [Ref. 5] determined that the decomposition rate is not affected by protracted drying (up to ten months), the presence of carbon dioxide, or mixing with metallic silver powder. Preliminary illumination appreciably raises the rate of decomposition at 100°C, and has somewhat less of an effect on disintegration at 118°C.

The size of the silver oxalate particles apparently has no particularly great effect on the decomposition rate. According to Benton and Cunningham, comminution slightly raises the decomposition rate. Macdonald, on the other hand, found that large crystals decompose at the same rate as precipitated preparations.

The effect of light apparently is of decisive importance in the study of decomposition under vacuum, but both in Macdonald's papers and in that of Benton and Cunningham [Ref. 5] there is no indication that the effect of dispersed light was entirely excluded either in the process of preparing and storing the materials, or in the experiments themselves.

The conflict between Macdonald's data, on the one hand, and those of Benton and Cunningham, on the other, with reference to the time dependence of the rate of silver oxalate decomposition follows even from the general shape of the curves. While it follows from Benton and Cunningham's findings that there is only one reaction maximum, according to Macdonald three kinds of maxima are observed on the rate-time curve. The first sort of maximum appears during decomposition under a layer of paraffin, as well as in specimens illuminated by ultraviolet light. By the time this maximum sets in, about 3% of the silver oxalate has decomposed.

The second sort of maximum is detected during "normal" decomposition in a vacuum in specimens previously illuminated by ultraviolet light. This maximum is substantially lower in specimens prepared by precipitation in an excess of silver nitrate, while it disappears entirely during decomposition in air or under a layer of oil.

The third sort of maximum is seen in decomposition under a layer of melted paraffin. It appears appreciably later than the second sort of maximum during "normal" decomposition.

The numerical relationship between reaction rate and decomposition time is described by Macdonald [Ref. 3] in two equations. Decomposition up to 3% (first process) is governed by the law

$$\frac{dx}{dt} = kt. \tag{1}$$

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Macdonald interprets this pattern as the growth of plane reaction nuclei beginning at the surface.

Most of the material (second process), according to Macdonald, decomposes by the exponential law

$$\frac{dz}{dt} = ae^{kt}.$$ (2)

Macdonald believes that the exponential relationship results from branching of the plane reaction nuclei, in which process the branching takes place on the crystal surface.

The third process, according to Macdonald, consists in branching of the plane nuclei both at the moment of interception of the crystal surfaces and at any point on the nucleus perimeter. This mechanism acts only in suppressing the second process. Macdonald states that in this case, too, the exponential relationship between reaction rate and time is valid.

Benton and Cunningham [Ref. 5] studied the kinetics of silver oxalate decomposition in the initial stage (up to 5-10%). They described the results of their investigations by the equation

$$V = at^m,$$ (3)

which is the first term of more complex kinetic equations deduced by B. V. Yerofeyev [Ref. 9] for the initial stages of reactions in which solid substances participate.

The value of m should theoretically be 4 in unilluminated specimens (reaction nucleus centers occurring at a constant rate) and m = 3 in specimens illuminated by ultraviolet (having point reaction-nucleus centers at the initial instant of decomposition).

Benton and Cunningham did, in fact, find m = 3.5 for the unilluminated specimens, but appreciably smaller values, as low as 1.4 in some experiments, for specimens preilluminated in ultraviolet light. Let us note that such low values of exponent m in equation (3) are easily explained on the basis of the theoretical derivation of kinetics equations which Yerofeyev [Ref. 9] gives as the result of growth of linear and plane nucleus centers.

The discrepancies between the kinetic relationships established by Macdonald and his collaborators, on the one hand, and Benton and Cunningham, on the other, have led these authors to differing interpretations of the reaction mechanism. While Macdonald insists on the chain nature of the process of plane nucleus development (see [Ref. 7], in particular) Benton and Cunningham describe the course of the reaction as the result of enlargement of three-dimensional reaction nuclei growing at a constant rate from point centers.

It is to be noted that in one of his articles Macdonald [Ref. 9] takes the possibility into account that the reaction takes its course through formation and growth of three-dimensional reaction nuclei.

This divergence in the interpretation of the reaction mechanism is of fundamental significance, because it is in general rather improbable that there are chain processes in the reactions of solid substances (e.g., see the pronouncements of Macdonald himself [Ref. 7] on this matter).

Benton and Cunningham's results, however, cannot be considered an entirely convincing proof that the reaction takes its course through formation and growth of three-dimensional nuclei, since they studied the reaction in a comparatively small sector (5-10%).

Kinetic analysis by means of equations like equation (3) is moreover inadequate. It is at present feasible to carry out kinetic analysis by improved means, in particular using equations like

$$\alpha = 1 - e^{-kt^n} \tag{4}$$

([Ref. 10], [Ref. 11]) which can describe the entire reaction.

The main task of our research was to study the kinetics of thermal decomposition of silver oxalate under the simplest conditions, uncomplicated by the action of any extraneous factors. We have attempted to explain whether the silver oxalate decomposition reaction is actually of a chain nature and thus stands apart from other thermal decomposition reactions of solid substances, or whether its course is the same as that of other reactions in which solid substances participate, i.e., proceeding via formation and growth of three-dimensional reaction nuclei.

The investigation method consisted of measuring the pressure of the carbon dioxide libertated during decomposition of silver oxalate at different temperatures. Particular attention was paid to elimina- /1105 tion of factors complicating the course of the reactions. Measures were taken, in particular, to eliminate the effect of light as much as possible, either in preparation and storage of the silver oxalate or in the course of the experiments themselves.

The present article reports the results of studying the kinetics of decomposition of pure silver oxalate. A subsequent article [Ref. 12] will give the results of investigating the kinetics of decomposition of solid solutions of silver oxalate in sodium oxalate.

Experimental Section

All the experiments to be described (preparation of silver oxalate and of its solid solutions in sodium oxalate [Ref. 12] and the decomposition itself of these preparations) were conducted under conditions of photographic darkness.

It may be assumed that the effect of light played no role in the present work.

Silver oxalate was made from chemically pure silver nitrate and sodium oxalate. Both materials were, before using, twice recrystallized. The silver nitrate solution (5 grams in 200 ml of water) was added by drops for 15 minutes into a solution of silver nitrate (4 parts in 600 ml of water) while stirring vigorously (300 mixer rpm). Temperature of the solutions during precipitation was kept at 25°C.

The silver oxalate precipitate was washed ten times by decantation and then several times in a Schott filter. It was dried and stored under vacuum over sulfuric acid. The same specimen was used in all experiments of the kinetics of decomposition of pure silver oxalate.

The equipment for studying the kinetics of silver oxalate decomposition consisted of a high-vacuum device, a MacLeod manometer, and a reaction tube in which was placed vial A with the weighed portion of $Ag_2C_2O_4$ (Figure 1).

The reaction tube was heated during the experiments in a glycerine thermostat whose temperature was maintained by means of a xylene heat regulator and an electronic relay with an accuracy of ± 0.2°C.

Conduct of experiments. The material (about 1 mg) was weighed out on a microbalance accurate to ± 0.005 mg. Weighing, like all other operations, took place under conditions of photographic darkness. The vial in which the weighed portion was placed was a thin-walled capillary tube sealed at one end. The vial was placed in the reaction tube and the tube was then evacuated to 10^{-6} mm Hg. At the same time a water bath heated to 60°C was set under the tube. At this temperature, evacuation went on for two or more hours until the "inleakage" (increase in pressure in the system when the pumps were disconnected) reached a value of less than 10^{-5} mm/min. When this was achieved, the reaction tube was turned on the ground-glass joint and moved from the water bath into the thermostat. This was considered to be the beginning of the experiment.

Pressure of the carbon dioxide liberated was read on the MacLeod manometer every 2 to 20 minutes, depending on reaction rate. The
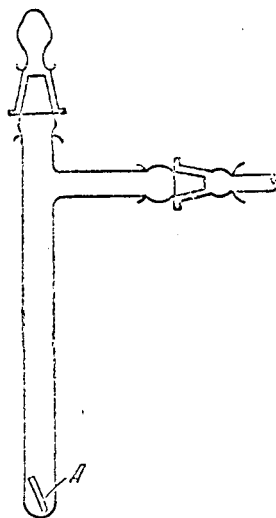
Figure 1

Reaction Tube

maximum carbon dioxide pressure reached during complete decomposition
of the weighed portion was no more than 1 mm. The reproducibility of
results in parallel kinetic experiments on silver oxalate decomposi-
tion was the same as for other reactions in which solid substances
take part. Maximum rate values in parallel experiments as a rule
differ by 10-20%.

Investigation Results

The kinetics of silver oxalate decomposition was investigated at
110, 115, 120, and 125°C. Most of the experiments were carried out
until decomposition reached 85-100%. Figure 2 gives the curves indi-
cating the dependence of the liberated carbon dioxide on time.

The experiments are numbered in accord with the sequence in which /1106
they were conducted. The missing experiment numbers refer to experi-
ments on decomposition of solid solutions of silver oxalate and sodium
oxalate which will be described in the next article [Ref. 12]. All
experimental results given here are converted for a portion weighing 1 mg.

The pressure-time curves given in Figure 2 are S-shaped. When
experimental data are represented as curves giving the dependence of
rate on time, the resultant curves have a shape characteristic of the
kinetics of reactions in which solid substances participate. First
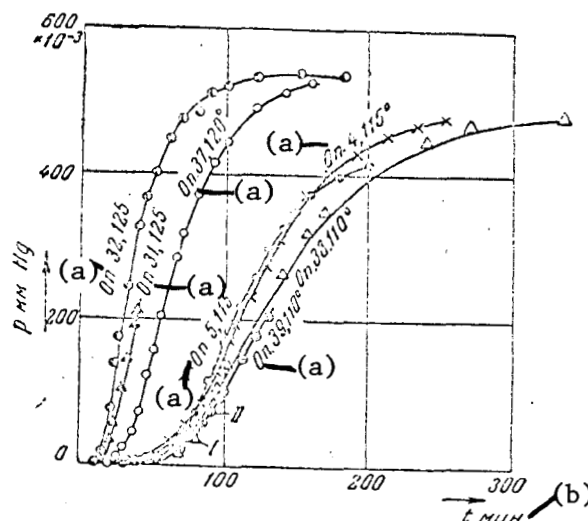
Figure 2

Pressure—Time Curves for $Ag_2C_2O_4$ Decomposition.
Interruptions in experiment 39: I - 60 minutes after start,
II - 30 minutes after resumption of experiment.

(a) Experiment; (b) t, min

the rate rises from a value close to zero, then it peaks, and, finally, falls. Figure 3 shows typical curves of this sort. The maximum rate is reached when decomposition is 27-38%. In none of the experiments /1107 were any supplementary maxima detected.

The first experiment was set up 48 hours after the silver oxalate was prepared. The next experiment at the same temperature 24 hours thereafter gave results differing from the first. The rate-time curve first rose more steeply than in the first experiment, but the maximum rate proved to be lower. Decrease in decomposition rate with specimen storage time continued for some time more. Only after 20 days did the decomposition rate practically cease to change. Apparently some re-crystallization process was going on during this period and affected the decomposition rate in the subsequent experiments.

Other investigators (Macdonald, Benton and Cunningham) working with silver oxalate do not mention this phenomenon. It is possible that the results of at least some of their experiments are incongruent with each other because of a change in the silver oxalate preparations during the investigation.
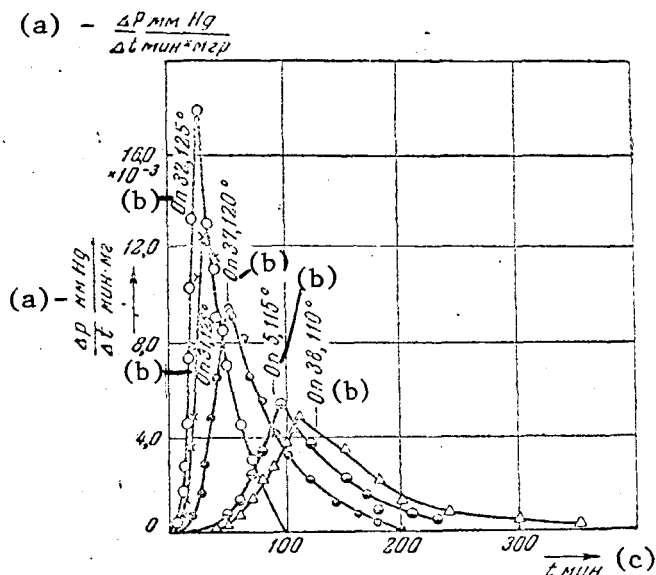
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Figure 3

Rate-time Curves for Silver Oxalate Decomposition at Various Temperatures

(a) - $\dfrac{\Delta P \text{ mm Hg}}{\Delta t \text{ min·mg}}$; (b) - Experiment; (c) - t, min

In order to resolve several questions which are discussed below, it seemed essential to study how the silver oxalate decomposition rate changes if decomposition which has already begun is interrupted and then started again.

For this purpose an experiment was set up at 110°C. The experiment was cut short by withdrawing the reaction tube from the thermostat in the 75th minute from the start of the experiment. By that moment the carbon dioxide pressure corresponded to 8% decomposition. The experiment was re-started 1 hour later; 15 minutes thereafter the reaction tube was again taken out of the thermostat. This time the interruption lasted 30 minutes. At the beginning of the second interruption, carbon dioxide pressure corresponded to 20% deocmposition. Both interruptions occurred before the moment of onset of the maximum rate at the temperature of 110°C. Figure 4 displays the results of this experiment (together with a parallel experiment at the same temperature, but without interruptions).

Here, time from the experiment's beginning is plotted along the axis of the abscissa. During this time the reaction tube was in the thermostat; in other words, this is the time with the interruptions left out. The points on the curve marked by pointers show where the interruptions
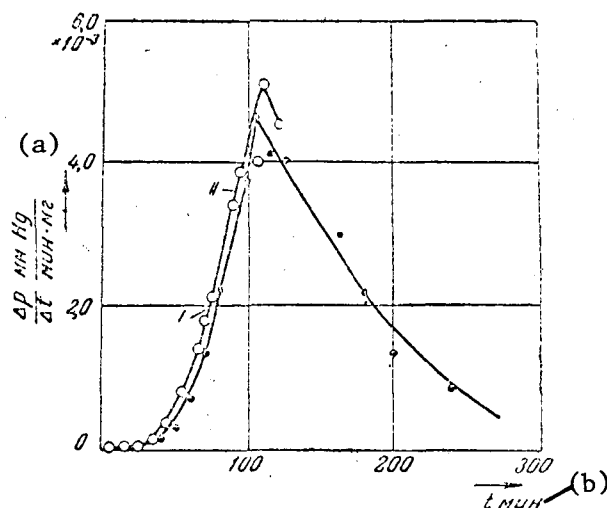
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(a)

Figure 4

Rate-time Curves for $Ag_2C_2O_4$ Decomposition at 110°C.

● - Experiment No. 38; 0 - Experiment No. 39 with interruptions:
I - 60 minutes after start, II - 30 minutes after resumption.

(a) - $\dfrac{\Delta P \text{ mm Hg}}{\Delta t \text{ min} \cdot \text{mg}}$; (b) - t, min

occurred. From the shape of the curve it is evident that the rate of decomposition after the interruption remains essentially the same as it was before interruption. The slight rate decrease after the first interruption may be satisfactorily explained by the reaction tube requiring a certain, although small, time to be heated up. It is very important that the general course of the curve, despite the two interruptions, is of the same nature as in the uninterrupted experiments.

As indicated above, Macdonald [Ref. 2] says that decomposition takes place in conformity with equation (2) before the rate maximum occurs. In order to check whether this pattern occurred in our experiments, the values of log p with respect to t were plotted on a graph. It is easy /1108 to see that, if equation (2) were applicable, there should be a rectilinear relationship between these variables:

$$\lg p = kt + \text{const.} \tag{5}$$

It was found that this relationship was not fulfilled. Only for the very beginning period of the reaction may we speak of a rectilinear

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Table 1

REGION OF APPLICABILITY OF EQUATION (5)

Experiment Number	Temperature, °C	Region of Applicability of equation (5) in Percentages of Total Decomposition
38	110	0—7
39	110	0—7
4	115	0—4
5	115	0—4
37	120	0—4
31	125	~0—2
32	125	~0—2

relationship between log p and t. Table 1 shows to what percentage of decomposition a rectilinear relationship prevails between log p and t.

In most of the experiments equation (5) is applicable only during the time corresponding to less than 4% decomposition. In two experiments alone did it amount to 7%.

Therefore, equation (5), and also equation (2), can describe only an insignificant initial portion of the whole process.

In the case of reactions passing through formation and growth of nuclei, the experimental data may in a significant segment of the curve be reproduced by an equation like

$$\alpha = 1 - \exp\left(-kt^n\right), \qquad (6)$$

where $\alpha = p/p_{00}$, while n (depending on shape and rate of formation /1109 of the reaction nuclei) varies from 4 to 6 and higher values [Ref. 10]. For short time values equation (6) changes into Benton and Cunningham's equation (3).

To study the applicability of this equation, it is advisable to represent it in logarithmic form:

$$\log\left[-\lg\left(1 - \alpha\right)\right] = n \log t + \log k. \qquad (7)$$

Figure 5 plots experimental findings on the kinetics of sliver oxalate decomposition in coordinates of $\log[-\log(1-\alpha)]$ with respect to log t.

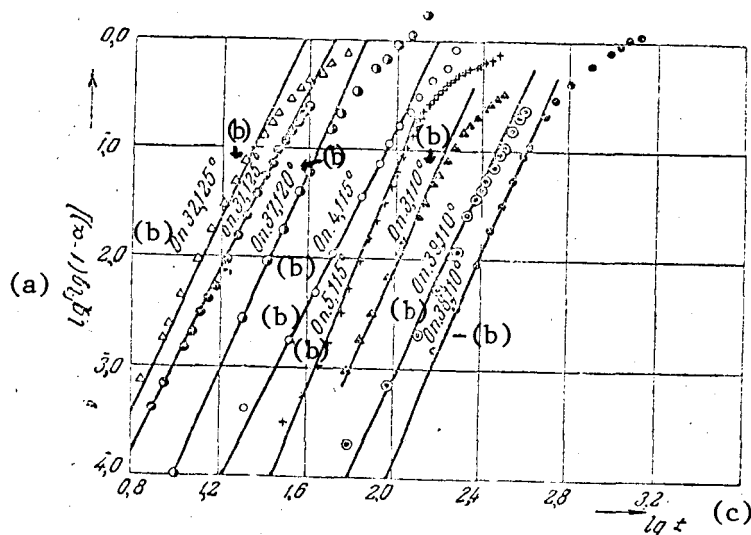Table 2 (Column 3) gives the value of the slope tangent (n) of a

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Figure 5

log[-log(1-α)] as a Function of t for Ag₂C₂O₄ Decomposition at
Various Temperatures. Curves for Experiments 3, 5, 38, and 39
Shifted to the Right by 0.2 (exp. 3), 0.1 (exp. 5), 0.6 (exp. 38),
and 0.5 (exp. 39).

(a) - log[-log(1-α)]; (b) - Experiment; (c) - log t

straight line drawn through the initial points. The values of n
fluctuate from 4 to 5.

Table 2 also gives the percentage values of decomposition up to
which equation (6) is valid. They are from 20 to 50%. From a comparison
of the limits of applicability of equation (6), on the one hand, and
equation (2) (Table 1), on the other, it follows that the region of equa-
tion (6) applicability is at least 5 to 7 times greater than the applic-
ability region of the exponential equation (2).

Discussion of Results

The above-described interruption experiment demonstrates, first of
all, that the rate of silver oxalate decomposition cannot be caused by
self-warming of the preparation because of the exothermic reaction effect.
The interruption in the experiment leads to cooling of the preparation,
but the rate after renewal of the experiment proves to be the same as
the preinterruption rate, nor can the concept of silver oxalate decomposi-
tion as a chain process be accommodated to this experimental fact. The

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Table 2

REGION OF APPLICABILITY OF EQUATION (6)

Experiment Number	Temperature °C	n	Log k	Region of Applicability of equation (6) in percentages of total decomposition
38	110	4,325	$\overline{10}$,30	0 — 50
39	110	4,26	$\overline{19}$,53	0 — 50
3	110	4,64	$\overline{11}$,54	0 — 11
4	115	4,12	$\overline{10}$,94	0 — 28
5	115	5,00	$\overline{11}$,20	0 — 14
37	120	4,65	$\overline{9}$,36	0 — 30
31	125	4,12	$\overline{8}$,92	0 — 20
32	125	4,42	$\overline{7}$,01	0 — 21

interruption periods in experiment 39 (60 and 30 minutes) are more than enough to dissipate completely the energy of the intermediate products — the carriers of a chain process. The only possible interpretation of the results of the interruption experiments is that a solid reaction product (silver) is formed during the silver oxalate decomposition reaction and that this silver is capable of accelerating decomposition. Mott [Ref. 8] and Gurney and Mott [Ref. 13] have examined the mechanism by which reactions including solid substances are accelerated by a product which is likewise solid.

A comparison of the applicability regions of equations (4) and (6) with data on kinetics (extending over 20-50%) and of equations (2) or (5) (extending over 2-7%) also makes it clear that the silver oxalate decomposition reaction has no chain nature, but proceeds via formation /1110 and growth of three-dimensional reaction nuclei which cannot be directly observed because of their submicroscopic size. The fact that equation (4) does not describe the entire reaction may stem from the fact that the reacting mass of silver oxalate crystals is not a perfectly homogeneous mass with respect to the process of reaction nuclei formation. A similar assumption, moreover, underlies the derivation of equation (4).

If the nuclei are to be generated at a constant rate [Ref. 10], exponent n must equal 4. It varies in fact from 4 to 5. The rise of the exponent to 5 may be explained by the idea underlying Mott's theory [Ref. 8]. According to Mott [Ref. 8], solid substance decomposition reactions which are catalyzed by the metal nuclei formed (Mott studies this reaction type by the example of the decomposition of azides) proceed as follows: At the metal to salt interface an electron leaps over from the anion to the metal, while the positively charged "hole" formed

at the site of the anion moves to the crystal surface by electrons from the adjacent anions leaping into the positive "hole". When the positive "hole" appears at the surface, the radical decomposes and escapes into the gaseous phase. The negatively charged metal nucleus, however, attracts the interlattice metal ions and therefore grows.

As for the generation of reaction nuclei, it is Mott's opinion [Ref. 8] that this process may be sketched in the following form: As a result of thermal energy fluctuation, an electron of an anion located on the surface goes over into the conductance zone and at a convenient opportunity is snatched by a positive "hole" formed on the surface after volatilization of the radical. Several (σ-) electrons may be needed to form a stable center.

The interlattice ions of the metal diffuse to the negatively charged center and, according to the above, cause it to grow.

The rising part of the kinetic curve should, according to Mott [Ref. 8], be described by equation

$$p = p_\infty k t^n \tag{8}$$

Formula (8) is derived from equation (4) by expanding the exponential in series and discarding all terms containing t except the first. According to Mott's initial treatment [Ref. 8], exponent n equals the number of electrons needed to form a stable initial center plus four:

$$n = \sigma + 4. \tag{9}$$

Somewhat later Mott [Ref. 13] identified σ with the number of positive ions needed to form a positive "hole" having lower potential energy levels of the electrons than in the conductance zone. We thus obtain $\sigma = 1$ for silver oxalate decomposition when n = 5.

With the smallest possible value $\sigma = 1$ according to Mott's theory, we obtain n = 5. Meanwhile, in experiments with pure silver oxalate n varies in value from 4 to 5.

Values of n below 5 are explained by Yerfeyev [Ref. 10]. Namely, the value of n may be reduced for the following two reasons.

First, the initial centers may not be point formations, but linear or plane formations. This is possible, for example, in cases when a positive "hole" on the crystal surface is a positive "small channel" situated, for example, along an edge of the crystal or crystallite, or, when it is a positive face.

In the case of linear centers and $\sigma = 1$, the kinetics equation will have the form

$$\alpha = 1 - e^{-kt^4} \tag{10}$$

or for the initial stage,

$$p = p_x \, k t^i.$$

(11)

The time t for "holes" representing positive planes will be included in the equation with the exponent 3.

Secondly, the number of electrons found in the conductance zones is, as Mott suggested, not proportional to time. That is, according to Mott,

$$n = \frac{SQ}{V},$$

(12)

where n is the number of conductance electrons, S is the crystal surface, V is volume, and Q is a constant for the given temperature.

The previous formula is derived if inverse recombination of electrons may be neglected. If, however, the recombination process cannot be neglected, then

$$\frac{dn}{dt} = \frac{SQ}{V} - k \cdot f(n, \nu),$$

(13)

where ν is the number of radicals formed on the surface as the result of electron migration into the conductance zone and not yet volatilized into the gaseous phase.

Assuming that $f(n, \nu) = n$ and that soon after start of the experiment a stationary state is established, we obtain

$$n = \frac{SQ}{V} k,$$

(14)

i.e., the number of electrons in the conductance zones, calculated per unit of volume, is constant. In this case the rate of initial center formation will be a value which does not depend on time for any number of electrons needed to form stable centers. That is,

$$\frac{dn}{dt} = \left(\frac{SQ}{Vk}\right)^a \cdot \text{const}$$

(15)

and

$$n = \left(\frac{SQ}{Vk}\right)^a t \cdot \text{const.}$$

(16)

In this case we will have the exponent n = 4 (since the rate of nuclei formation per unit of volume of the unreacted material is constant) when there are positive point "holes" and, accordingly, with a lower power of t when there are linear and plane positive "holes".

It is at present impossible to ascertain with accuracy which of these two main reasons lowers the exponent n in equation (4) for the silver oxalate decomposition which we have investigated.

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Temperature Dependence of Silver Oxalate Decomposition Rate

The values of the constant log k (from equation [4]) in experiments at different temperatures were calculated to determine the temperature dependence of the silver oxalate decomposition rate. Table 2 (column 4) gives the computed values.

When computing the activation energy, we must take the fact into consideration that the values of k or of log k derived correspond to different exponents n in equation (4), which Table 2 indicates as varying from 4 to 5. In view of the inconstancy of the n values in the different experiments it is, strictly speaking, impossible to use the ordinary graphic method of calculating activation energy by utilizing the findings of all the experiments. Since, however, in experiments 3 (at 110°C) /1112 and 37 (at 120°C) the respective values of n are practically the same (4.64 and 4.65) the findings of these two experiments may be employed to compute activation energy.

We have

$$E = R \frac{T_1 T_2}{T_1 - T_2} \lg \frac{k_1}{k_2} = 125\,000 \text{ cal.}$$

An identical n value of 4.12 also occurs in experiments 4 (at 115°C) and 31 (at 125°C). From this pair of equations we find in similar fashion

$$E = 140\,000 \text{ cal.}$$

The average value of E from these two experimental findings will be

$$E = 132\,500 \text{ cal.}$$

When calculating the activation energy graphically by using the findings of all the experiments, which, as noted above, is not rigorous, we derive a figure which is close to that found, i.e., 133,500 cal.

As the final value we adopt

$$E = 133\,000 \text{ cal.}$$

The computed activation energy is a composite value, that is,

$$E = E_w + 3E_u, \tag{17}$$

where E_w is the activation energy of the process by which reaction centers are formed and E_u is the activation energy of the process of linear nuclei growth (e.g., see Mott [Ref. 8]).

Conclusions

1. The kinetics of thermal decomposition of silver oxalate under

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conditions of photographic darkness has been experimentally studied.

2. It has been established that the kinetics of decomposition is represented over the first 20-50% by the equation

$$\alpha = 1 - \exp(-kt^n),\qquad(4)$$

where n equals 4 - 5, and that the solid product formed during the reaction catalyzes the reaction.

3. It has been shown that the kinetic findings do not match Macdonald's chain theory, but corroborate the conception of the reaction mechanism as a process of generation and growth of submicroscopic three-dimensional reaction nuclei.

4. The value of the exponent n in equation (4) has been explained on the basis of Mott's theory.

5. It has been shown that the number of positive ions needed to form the initial center of growth of a nucleus of metallic silver is 1.

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REFERENCES

1. Macdonald, J.Y., Hinshelwood, C. Journ. Chem. Soc., London, 127, 2764, 1925.
2. Macdonald, J.Y. Journ. Chem. Soc., London, 832, 1936.
3. Macdonald, J.Y. Journ. Chem. Soc., London, 839, 1936.
4. Macdonald, J.Y., Sandison, R. Trans. Far. Soc.,34, 589, 1938.
5. Benton, A., Cunningham, G.L. Journ. Am. Chem. Soc.,57, 2227, 1935.
6. Macdonald, J.Y. Journ. Chem. Soc., London, 273, 1937.
7. Macdonald, J.Y. Trans. Far. Soc.,34, 977, 1938.
8. Mott, N.F. Proc. Roy. Soc.,A, 172, 325, 1939.
9. Yerofeyev, B.V. Zhurnal Fizicheskoy Khimii, 9, 827, 1937.
10. Yerofeyev, B.V. Doklady Akademii Nauk SSSR,52, 515, 1946.
11. Kolmogorov, A.N. Izvestiya Akademii Nauk SSSR, Seriya Matematiki, No. 3, p. 355, 1937.
12. Bel'kevich, P.I., Yerofeyev, B.V., and Volkova, A.A. [In press.]
13. Gurneya, R.W., Mott, N.F. Electronic Processes in Ionic Crystals. Oxford, 1940.